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Continuum mechanics modelling and simulation of carbon nanotubes.

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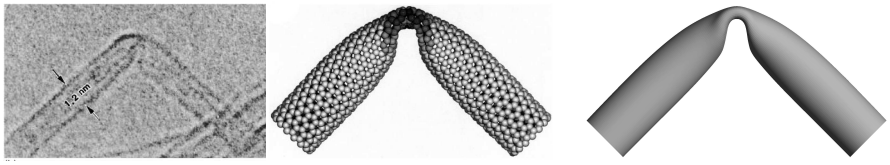
Abstract. The understanding of the mechanics of atomistic systems greatly benefits from continuum mechanics. One appealing approach aims at deductively constructing continuum theories starting from models of the interatomic interactions. This viewpoint has become extremely popular with the quasicontinuum method. The application of these ideas to carbon nanotubes presents a peculiarity with respect to usual crystalline materials: their structure relies on a two-dimensional curved lattice. This renders the cornerstone of crystal elasticity, the Cauchy-Born rule, insufficient to describe the effect of curvature. We discuss the application of a theory which corrects this deficiency to the mechanics of carbon nanotubes. We review recent developments of this theory, which include the study of the convergence characteristics of the proposed continuum models to the parent atomistic models, as well as large scale simulations based on this theory. The latter have unveiled the complex nonlinear elastic response of thick multiwalled carbon nanotubes, with an anomalous elastic regime following an almost absent harmonic range.

Keywords: Continuum mechanics, carbon nanotubes, finite elasticity, atomistic models, nanotube-based devices

1. Introduction

Carbon nanotubes (CNTs) can be viewed as graphene sheets (a two-dimensional hexagonal lattice of carbon atoms) wrapped into cylinders one atom thick of specific chirality and diameter. Although irradiation or the synthesis process can produce defects into the crystal structure, these nanostructures are remarkably perfect. Since their discovery in 1991 [18], carbon nanotubes have attracted much attention due to their unique structure and mechanical, chemical and electronic properties [11]. These properties have made of carbon nanotubes the central element in an array of nano-structured materials, as well as nano-sensors and devices. Mechanics plays a central role in nanotube-based nanotechnology. On the one hand, the exceptional mechanical properties (a nominal Young's modulus of 1 TPa, ideal strength of over 100 MPa)



Iijima et al. (1996)

Figure 1. Buckling at the nanoscale: experimental observation, atomistic calculation (Reprinted with permission from Iijima, S., C. Brabec, A. Maiti, and J. Bernholc: 1996, Structural flexibility of carbon nanotubes. *Journal of Chemical Physics* **104**(5), 2089-2092. Copyright 1996, American Institute of Physics.) and exponential Cauchy-Born rule-based continuum calculation

has prompted intense research in nanostructured materials such as nanotube-based nanocomposites. On the other hand, the strong function of other properties such as electrical conductance [37] or chemical reactivity [33] with deformation has deep implications in the design of nanotube-based devices and sensors.

From a mechanics viewpoint, the strong crystalline network together with the hollow cylindrical geometry confers carbon nanotubes with features of strong crystalline solids as well as features of flexible macromolecules, with a very rich nonlinear elasticity. Indeed, similarly to bulk crystalline solids, deformation and failure is mediated by plasticity and fracture when the in-plane behavior of graphene is probed. Theoretical studies suggest that strain relaxation in deformed nanotubes can occur through plastic activity–a Stone-Wales defect acts as a dislocation dipole that splits into two dislocations that can glide [26]. More importantly, fracture of nanotubes subject to tension has been reported experimentally [40], and theoretical work has highlighted the importance of preexisting defects in the fracture behavior of nanotubes [25]. The mechanical failure of nanotubes bears particular relevance with regards to nanostructured materials that try to exploit the strength of carbon nanotubes. On the other hand, the three-dimensional film structure makes of nanotubes extremely flexible nanostructures; they can sustain very large distortions in a reversible manner [13, 37]. Transmission electron micrographs as well as atomistic simulations show that when severely deformed, carbon nanotubes tend to buckle displaying morphologies remarkably reminiscent of macroscopic buckled shells [19], Fig. 1. This flexibility and resilience offers opportunities for devices and sensors. The combination of super-high stiffness and strength and high flexibility makes of nanotubes unique mechanical systems.

Since the pioneering work of Yakobson and co-workers [39], who first explicitly acknowledged the analogy between the mechanics of carbon

nanotubes and the continuum elasticity of shells, the use of continuum mechanics concepts in nanotube mechanics has become common practice. Continuum mechanics rationalizes the mechanics of materials in terms of irreducible sets of parameters (e.g. elastic moduli, Peierls stress), is amenable to analytical calculations, and affords very efficient simulations (e.g. finite elements). The most classic approach for continuum modelling of atomistic systems adopts a standard continuum theory (e.g. linear elasticity), and adjusts the material parameters to the data available. This phenomenological approach is simple and useful, particularly when the mechanics are well understood *a priori*, and the phenomena are simple enough to be encoded in the model. This approach has enjoyed great popularity for nanotubes, which have been modelled as thin elastic shells [32, 39], classical elastic beams [30], and non-local elastic beams that intend to capture the wave dispersion behavior of nanotubes [38] to name a few . While this type of methods have been extended to the finite deformation regime [27], the reduced number of fitted parameters raises doubts on the appropriateness of these models when material nonlinearities are important. This point is further developed in the paper. Another approach to continuum modelling of crystalline materials aims at deductively constructing continuum theories starting from models of the interatomic interactions as realistic as possible, with a minimal set of assumptions [34, 35]. In the present work, we will follow this path.

The paper is organized as follows. We first briefly outline the bottom-up approach to crystal elasticity based on the Cauchy-Born hypothesis, and the extension proposed to capture the curvature of lattices of reduced dimensionality. The simple yet nontrivial example of an atomic chain deforming in 2D is developed in detailed, and for this model, an asymptotic and numerical study of the relationship between continuum and atomistic models is reported. Then, examples of the application of the theory to the simulation of carbon nanotubes are presented, which include large scale simulations which help understand the complex mechanics of thick multi-walled carbon nanotubes (MWCNTs). Finally the conclusions and outlook are summarized.

2. Continuum modelling of curved lattices

2.1. The Cauchy-Born hypothesis

The essential idea behind the present theory, as in classical finite crystal elasticity, is to use the Cauchy-Born rule [12] (here a generalized CB rule) to express the geometric quantities characterizing the deformation of the lattice in terms of the deformation of the continuum. For

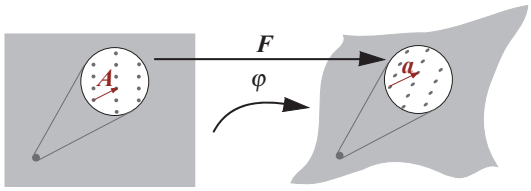


Figure 2. The standard Cauchy-Born rule for space-filling crystals: the undeformed body is subjected to a deformation map φ, whose linear part, the deformation gradient $\mathbf{F}$ transforms locally the underlying lattice

space-filling crystals, the central hypothesis behind molecular theories of nonlinear elasticity is that, at the scale of the atomic spacing, the deformation of the crystal is homogeneous. Therefore, locally, the crystal is subjected to an homogeneous deformation characterized by the deformation gradient $\mathbf{F}$, which transforms the undeformed lattice vector $\mathbf{A}$ into $\mathbf{a} = \mathbf{F}\mathbf{A}$ (see Fig. 2). This relation allows us to express geometric quantities such as bond lengths and bond angles, which enter as arguments in the inter-atomic potentials, in terms of the right Cauchy-Green deformation tensor. By averaging over the crystal unit cell, it is straightforward to formulate a continuum hyper-elastic constitutive relation explicitly in terms of the atomistic potential. This systematic approach produces constitutive models which inherit the symmetries of the underlying lattice, and can be used to assess the onset of material instability [17] or as the basis for efficient finite element simulations [35, 36]. Some authors interested in the mechanics of carbon nanotubes have used the standard crystal elasticity theories to describe the in-plane behavior of the wall (i.e. the mechanics of graphene), and study the elasticity and onset of failure [41].

The Cauchy-Born rule is a kinematic hypothesis, whose validity can be checked a posteriori, for instance by comparing with direct atomistic calculations. In the absence of defects, or emergence of microstructure, this hypothesis has been found to accurately predict the nonlinear elasticity of bulk crystals. The treatment of complex lattices requires some extra care [10, 36, 2]. Also recently, there has been work on the mathematical analysis of this hypothesis, focusing on interesting cases in which it fails (see for instance [16]).

2.2. Exponential Cauchy-Born rule

Now consider a curved crystalline solid of reduced dimensionality, such as the graphene monolayer. It is natural to treat the equivalent continuum as a solid of reduced dimensionality, e.g. a surface without thickness in the case of a crystalline film. Indeed, the two-dimensional nature of the lattice does not suggest any mechanically meaningful

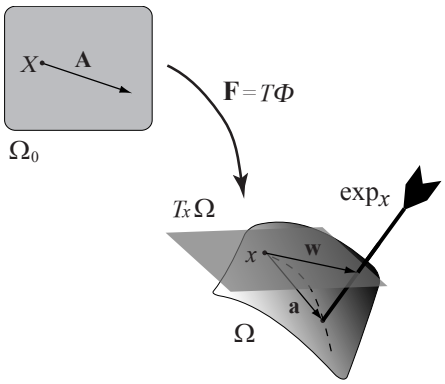


Figure 3. Illustration of the surface kinematics and the exponential Cauchy-Born rule. The exponential map transforms the vector $\mathbf{w} = \mathbf{FA}$ tangent to the surface into a chord of the surface $\mathbf{a}$.

thickness [4]. As illustrated in Fig. 3, in this kinematic setting the standard Cauchy-Born rule produces deformed lattice vectors which are tangent to the surface. However, deformed lattice vectors should be chords of the surface, i.e. connecting two atoms on the surface. In [2] it was recognized that the standard Cauchy-Born rule does not capture the curvature of the film, and a generalized kinematic rule was proposed exploiting the natural map between the tangent of a manifold and the manifold itself provided by the exponential map. By composing the exponential map with the standard Cauchy-Born rule

$$\mathbf{a} = \exp_x \mathbf{FA} \tag{1}$$

we define the so-called exponential Cauchy-Born (ECB) rule, which leads to expressions of the deformed lattice measures in terms of the stretch (first fundamental form) and the curvature (second fundamental form) of the surface, has been shown to correct the deficiencies of the standard rule for curved lattices, and to lead to accurate models [5].

For the sake of clarity, let us describe the resulting continuum theory in the simplest nontrivial example of an atomic chain containing N atomic bonds and deforming in two dimensions (see Fig. 4). The discrete atomistic potential for this system has a bond stretch contribution and a three-body contribution:

$$\mathcal{E}_{\text{atom}} = \sum_{\text{bonds}} \mathcal{V}_s(a_i) + \sum_{\text{angles}} \mathcal{V}_\theta(\theta_j) \tag{2}$$

$$= A \left[\sum_{\text{bonds}} \widetilde{\mathcal{V}}_s \left(\frac{a_i}{A} \right) + \sum_{\text{angles}} \widetilde{\mathcal{V}}_\theta \left(\frac{\theta_j - \pi}{A} \right) \right]. \tag{3}$$

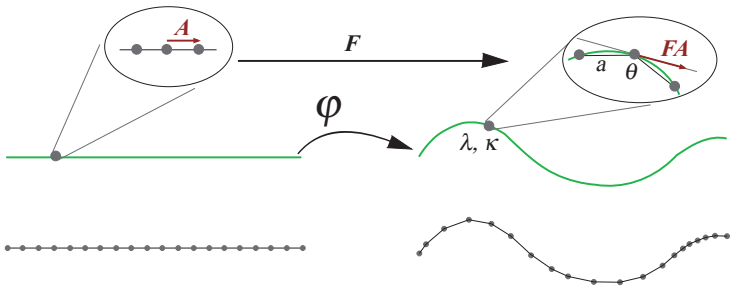


Figure 4. Illustration of the continuum and discrete models for the toy example of an atomic chain in 2D

The potential energy has been rewritten in the last part of the equation for convenience. We consider two- and three- body potentials that need not be harmonic.

The local approximation of the exponential Cauchy-Born rule in this simple setting produces the following relations between the discrete deformation measures, namely the bond length a and the angle between adjacent bonds θ, and the continuum strain measures, i.e. the stretch λ and the curvature κ of the deformed curve with respect to the undeformed initially straight body [1]:

$$a(\lambda,\kappa) = \frac{2}{\kappa}\sin\frac{\lambda\kappa A}{2}; \quad \theta(\lambda,\kappa) = \pi - \lambda\kappa A \tag{4}$$

where A denotes the undeformed bond length (see Fig. 4). By plugging these expressions into the atomistic potential, and averaging over a unit cell of length A, the equivalent continuum is a curve (initially straight and of length $L = NA$) whose energy is

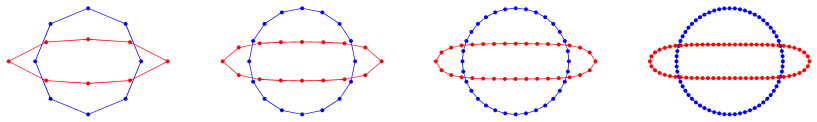
$$\mathcal{E}_{\text{cont}} = \int_0^L W_{ECB}(\lambda(X),\kappa(X))\, dX \tag{5}$$

with the strain energy density

$$W_{ECB}(\lambda,\kappa) = \widetilde{\mathcal{V}}_s\left(\frac{a(\lambda,\kappa)}{A}\right) + \widetilde{\mathcal{V}}_\theta\left(\frac{\theta(\lambda,\kappa)-\pi}{A}\right). \tag{6}$$

2.3. Relationship between discrete and continuum

The methods of crystal elasticity bridge atomistic descriptions of matter and finite deformation elasticity. If the crystal is simple, stable, free of defects or microstructure, and is homogeneously deformed, then the methods based on the Cauchy-Born rule are exact. In other situations, for instance when solving a boundary value problem (minimizing the



$$A_\varepsilon = \varepsilon A, \quad A_\varepsilon N_\varepsilon = L, \quad \widetilde{\mathcal{V}}_{\theta,\varepsilon}(\cdot) = \varepsilon \widetilde{\mathcal{V}}_\theta\left(\frac{\cdot}{\varepsilon}\right), \quad \widetilde{\mathcal{V}}_{s,\varepsilon}(\cdot) = \varepsilon \widetilde{\mathcal{V}}_s\left(\frac{\cdot}{\varepsilon}\right)$$

Figure 5. Sequence of atomistic problems used to assess numerically the convergence of continuum models.

potential energy of a crystal subject to loads and boundary conditions), the relationship between the atomistic solution and that provided by the continuum model with the Cauchy-Born constitutive relation is not so clear. The mathematical community has addresses this issue by investigating in what sense continuum models arise as asymptotic limits of discrete models (see for instance [6, 7]). Typically a sequence of re-scaled atomistic problems is considered, and the emergence of a continuum model in the limit is established. The re-scaling of the problems can be understood as the though experiment of making the atomic spacing smaller and smaller at fixed size of the body (large body limit). In [6], this limit was performed assuming that the continuum and the atomistic deformations are equal wherever both are defined, while in [7] it was proven that the solutions of the sequence of discrete problems (minimizers of the relevant discrete energies) converge to the solution of a continuum problem through Γ-convergence techniques.

In the present section, we provide the asymptotic continuum limit of the chain model described above, extending part of the analysis of [6] beyond the nearest neighbor. Then the convergence of the minimizers for a given example is established numerically, which provides information on the *convergence* of the discrete model to different continuum models. More details about this analysis will be provided elsewhere.

We first consider the sequence of re-scaled problems depicted in Fig.5; a circular chain of fixed extended length L is stretched by 50% laterally by pulling two atoms in a diameter. Starting from a reference model with atom spacing A and $N = L/A$ atoms, a sequence of models with atomic spacing $A_\varepsilon = \varepsilon A$ and $N_\varepsilon = N/\varepsilon$ atoms is considered, with energy

$$\mathcal{E}_{\text{atom},\varepsilon} = \varepsilon A \left[\sum_{\text{bonds}} \widetilde{\mathcal{V}}_s\left(\frac{a_i}{\varepsilon A}\right) + \sum_{\text{angles}} \widetilde{\mathcal{V}}_\theta\left(\frac{\theta_j - \pi}{\varepsilon A}\right) \right].$$

Adapting the ideas in [6] to the present setting, and by noting that

$$\frac{a_i}{A} = \lambda + \mathcal{O}(A) \quad \text{and} \quad \frac{|\theta_j - \pi|}{A} = \lambda\kappa + \mathcal{O}(A),$$

a hyper-elastic continuum model for a line with strain energy

$$W_{asymp}(\lambda, \kappa) = \widetilde{\mathcal{V}}_s(\lambda) + \widetilde{\mathcal{V}}_\theta(\lambda\kappa) \tag{7}$$

arises in the limit as $\varepsilon \to 0$ under the hypothesis that the atomistic and the continuum deformations coincide wherever they are both defined, and some regularity hypothesis.

We can now ask ourselves whether the actual solutions of the sequence of atomistic problems converge to the solution of a continuum problem with the strain energy density of Eq. (7). Mathematically, this is answered through Γ-convergence techniques [7]. Here, we investigate this convergence numerically, by actually solving the sequence of atomistic problems, and the continuum problem with an overkill discretization. The left plot in Fig. 6 shows the convergence of the relative difference between the atomistic equilibrium energy for several values of ε and the continuum equilibrium energy for the asymptotic model. It can be observed that indeed the solutions of the re-scaled atomistic problems converge to the solution of the asymptotic continuum model. Note that the continuum model based on the exponential Cauchy-Born hypothesis, with the strain energy density in Eq. (6), seems to be out of the picture. Unlike the asymptotic model, this model does depend on the atomic spacing, and therefore for different values of ε the resulting continuum problem is different. The left plot of Fig. 6 shows that as $\varepsilon \to 0$, the continuum model based on the exponential Cauchy-Born rule converges to the asymptotic model.

While this analysis provides useful information (it shows that, in the limit of vanishing atomic spacing, the models agree), it does not address a more interesting question from a practical viewpoint: how does a continuum model reproduce the parent atomistic model at finite, or even large, values of the atomic spacing (relative to the body size)? To address numerically this issue, we plot the relative difference of the energy provided by the continuum models (the asymptotic limit and the ECB model) and that provided by the atomistic model (right plot of Fig. 6). This plot shows for both continuum models, the relative error with respect to the atomistic solution decreases as $\varepsilon \to 0$ with a rate of convergence of 2. It can also be observed that the ECB model always provides more accurate representations of the atomistic model as compared with the asymptotic model, particularly for large values of ε.

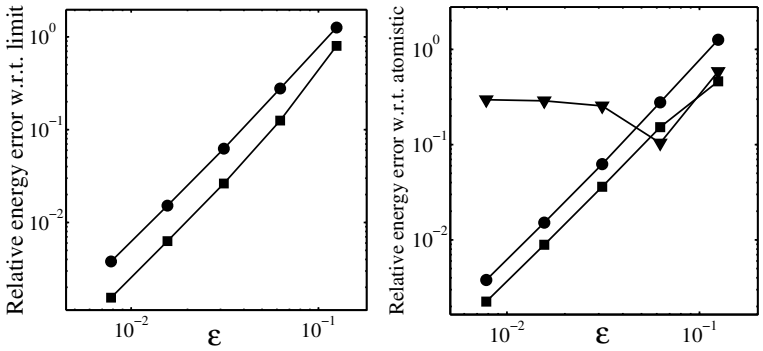


Figure 6. Numerical study of the convergence of several continuum models for an anharmonic potential. Left: convergence of the atomistic model (•) and the ECB model (■) to the limit asymptotic model. Right: convergence of the asymptotic (•), the ECB (■), and WLC (▼) continuum models to the atomistic model.

We also consider a third continuum model characterized by the strain energy density typical of the worm-like chain (WLC) model

$$W_{WLC}(\lambda,\kappa) = \frac{1}{2}k_s(\lambda-1)^2 + \frac{1}{2}k_\theta\kappa^2, \tag{8}$$

where the elastic moduli k_s and k_θ are matched to the infinitesimal elastic response of the atomistic chain. This model, while harmonic in the strain measures, is (geometrically) nonlinear. This kind of phenomenological model has the same spirit of the continuum models for carbon nanotubes based on geometrically nonlinear shell models and a parameter fit for the elastic response (see e.g. [27]). As can be observed in the right plot, this model does not converge to the atomistic model. Thus, while qualitatively correct and capturing the geometric nonlinearities, this model is unable to correctly capture the material nonlinearities arising from the atomistic potentials.

Thus, we have seen that given an atomistic model, there are several appropriate continuum models which can be considered. These include the asymptotic limit model W_{asymp}, but also the model based on the ECB hypothesis W_{ECB} and possibly other models that we have not considered. We have provided a procedure to compare the relative performance of the different continuum models with respect to parent atomistic model, and have seen that for the examples considered, the ECB model outperforms the asymptotic model. The results also show that a naive yet reasonable phenomenological model based on parameter fitting does not converge to the atomistic model. To conclude this section, it should be carefully noted that while for the simple example of the atomic chain the asymptotic model can be easily obtained, it is not straightforward to obtain an asymptotic model for a system like

graphene and general inter-atomic potentials (e.g. the Brenner potential [8]). On the contrary, a model based on the ECB hypothesis is always straightforward to formulate, once the basic link between bond lengths, bond angles, dihedral angles, etc, and the continuum stretch and curvature is established.

3. Application to carbon nanotubes

When applying continuum mechanics concepts to nano-scale systems, one should carefully account for effects usually negligible at the macro-scale, which nevertheless can become very important at small scales. In particular, surface effects can become dominant, and the thermal motions can produce a non-negligible entropic contribution to the free energy of a coarse-grained system. For carbon nanotubes, the first of these effects is crucial, since nanotubes are "all surface", and interact through non-bonded forces with their surroundings. The continuum modelling presented here includes a continuum version of the non-bonded interactions, as detailed in [2]. As for the effect of the thermal motions, due to the high stiffness of the carbon-carbon bond in graphene, at room temperature these effects become negligible for applications, and are usually ignored. This point may be debatable when probing the flexural stiffness of graphene, which is quite compliant to these kinds of deformations. For example, the energy of a relaxed $(10, 10)$ nanotube relative to the ground energy of planar graphene, i.e. the energy required to wrap the sheet into the cylindrical shape, is only three times larger than $k_B T/2$.

For the details on the formulation and implementation of the ECB theory to carbon nanotubes, which includes the so-called *inner displacements* to account for the fact that graphene is a complex lattice, see [5]. In this reference, an exhaustive comparison is made between the results provided by the continuum theory discretized by finite elements and independently run atomistic calculations, for problems involving very large deformations and structural instabilities. One of these comparisons for a twisted nanotube is reported in Fig. 7. The morphological agreement for the deformed atomistic and continuum models is remarkable despite the large distortions, and an excellent agreement is also achieved for the energetics (compare continuous line and bullets). It should be noted that the atomistic potential used, the Brenner potential [8], allows for bond-breaking. For this example, despite the large deformations, the structure remains elastic, highlighting the extent to which properly formulated models of nonlinear elasticity provide faith-

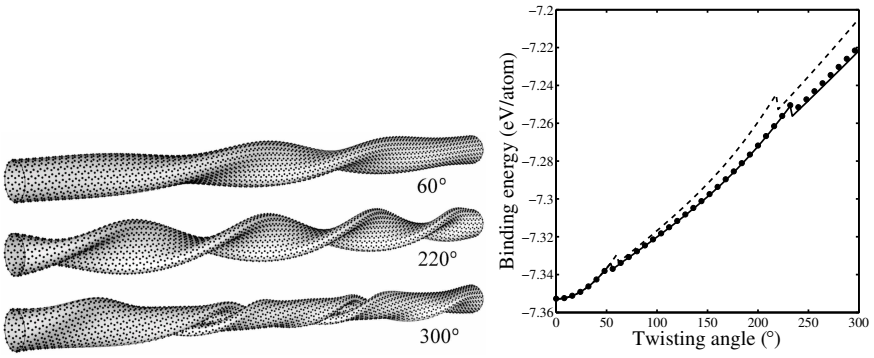


Figure 7. (a) Twisted 25.11 nm long (10,10) nanotube: super-imposed deformed configurations at three twisting angles for atomistic calculation (black spheres) and continuum finite element calculation (gray surface). (b) Comparison of the strain energy as a function of the twisting angle for atomistic calculation (—), and continuum/FE calculation (•), and strain energy evolution for the simplified model (- - -).

ful models for the mechanics of nanotubes. For an alternative purely computational approach, see [31].

A continuum theory for nanotubes allows us to easily access computationally larger systems directly relevant to device design and analysis. This capability is exploited in the examples presented later in this paper. The continuum model also provides a deeper understanding on the mechanics of nanotubes, and more specifically the relationship between the elasticity and the inter-atomic potential. In [4], the explicit expression between the elastic moduli of the graphene sheet and the functional form of the inter-atomic potential were provided. While the in-plane elastic moduli in the planar configuration follow from the standard methods, the elasticity theory based on the exponential Cauchy-Born rule provided the relationship between the flexural stiffness of the wall and the atomistic model. This result shows, for instance, that a naive model for graphene based on a standard two-body/three-body expansion of the energy around the ground planar state produces a model with zero initial bending stiffness.

3.1. What about simpler models?

When interrogating the quality or appropriateness of a continuum model, one should bear in mind what is expected from that model. What can be expected from a continuum model ranges from a simple framework for the interpretation of experiments/atomistic calculations, to its use for the predictive simulations of complex phenomena.

Although the continuum models described above affords very accurate and efficient computations, it is relatively complex as compared with standard engineering material models; it is strongly non-linear, its evaluation requires the inner displacement relaxation, and the membrane and bending contributions are tightly coupled. On the other hand, the simulations suggest that the nonlinearity of the mechanical response is mostly geometrical, rather than stemming from the material model. Recently, some authors have studied the nonlinear mechanics of carbon nanotubes through standard nonlinear elastic shell models, fitting the material parameters to available data (see for instance [27]). Although these models include a material parameter of controversial nature, namely the thickness of a two-dimensional arrangement of atoms, they found good qualitative agreement with experiments. This prompts the question of whether simpler models are sufficient.

In this section, a simple and well motivated nonlinear elastic model with an irreducible set of elastic parameters that does not involve any wall thickness is considered. It is well known that the infinitesimal in-plane elastic response of graphene is isotropic. In [4] we showed that the bending response is also isotropic. By analogy with the Kirchhoff-Saint Venant model of finite elasticity, the simplest isotropic model for a two-dimensional continuum splits the energy into membrane and bending energy, and is the higher dimensional generalization of the model in Eq. (8). It is of the form

$$W_{\text{approx}} = W_{\text{m}} + W_{\text{b}} = \frac{1}{2}[2\mu \mathbf{E} : \mathbf{E} + \lambda(\text{tr } \mathbf{E})^2] + \frac{1}{2}[a(2H)^2 + bK]$$

where μ and λ are the 2D Lamé coefficients [4], $\mathbf{E}$ is the Green strain tensor, the mean curvature H and the Gaussian curvature K are the invariants of the curvature tensor, and a and b are bending elastic moduli. Since $\int_\Omega K \; dX$ is a topological invariant of the surface, the term involving K can be disregarded from the strain energy density. In [4] we provided explicit expressions for the bending modulus a in terms of the inter-atomic potential, as well as for the Lamé coefficients. Figure 7(b) (dashed line) shows that indeed this simple model captures the essential geometric nonlinearities of the problem, and provides quite good energetics although a systematic drift can be observed. It also shows that for large deformations, when presumably the material nonlinearities become more important, this model does not perform as well as the complete model discussed above. Although not shown, the agreement in the deformed configurations is also reasonably good for the simplified model, although visual discrepancies are noticeable.

Thus, despite the relatively good agreement between a simple elastic model with a few material parameters, a quantitative agreement with

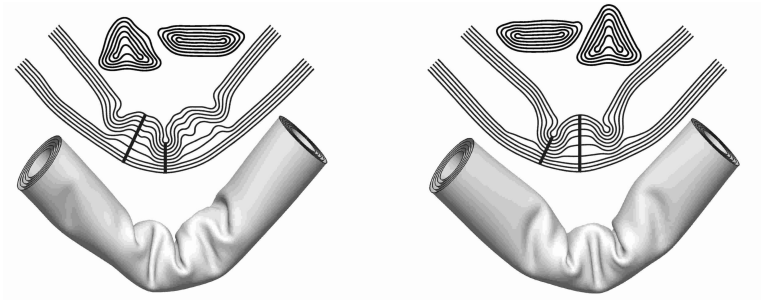


Figure 8. Example of metastability in nanotube-systems; the two configurations, while morphologically very different, are nearly undistinguishable from the energetic viewpoint.

the atomistic system can only be accomplished through atomistic-based continua which naturally account for the material nonlinearities arising at large strains. Besides, the predictive ability of phenomenological models beyond the regime in which the parameters were fit is always a concern.

3.2. Behavior of thick MWCNTs: from atoms to devices

As a prelude to the behavior of thick MWCNTs, let us consider first a 5-walled CNT. We have seen in Fig. 1 that bent single-walled carbon nanotubes tend to form single buckles which concentrate most of the deformation. When larger multiwalled tubes are considered, like the 5-walled nanotube in Fig. 8 (see also [19, 5]), typically the mechanical response becomes more complex; more buckles can be observed, and the numerical experiments produce a number of meta-stable configurations (which follow from the bifurcation of the equilibrium path) nearly undistinguishable energetically, but nevertheless quite different morphologically.

The efficient and reliable computational method based on the exponential Cauchy-Born rule and finite elements allows us to study easily multi-million atom systems of thick MWCNTs with models containing two orders of magnitude less degrees of freedom. These simulations contribute to the understanding of the mechanics of thick MWCNTs, currently serving as structural building blocks in an array of nano-scale devices [30, 29, 14]. Previously, these systems were analyzed qualitatively by simplified 2D anisotropic elasticity models [22], macroscopic rubber scrolls and geometric scaling arguments [24], or phenomenological shell models [27]. In [3], we presented reliable simulations based on realistic potentials which revealed the 3D morphological structure of the experimentally observed rippling deformations [30, 20, 23] analogous to

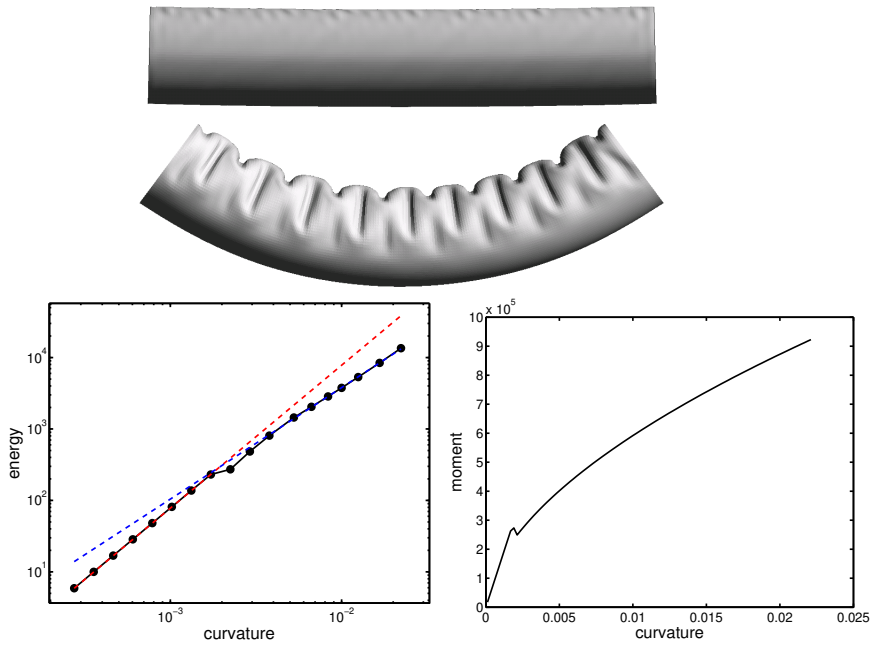


Figure 9. Anomalous elasticity of thick MWCNTs subjected to bending (here a 80 nm long 20-walled CNT.

the Yoshimura pattern. But the most important result of this study is the identification of two distinct elastic regimes in the mechanical response of thick MWCNTs; initially, these systems behave harmonically, displaying a quadratic growth of the strain energy with deformation, which is followed by a non-trivial well-defined scaling of the energy. The initial harmonic regime is practically absent for thick MWCNTs, and the latter anomalous and genuinely nonlinear structural response dominates the mechanical behavior for moderate and large deformations, such as those encountered in oscillators and devices. The energetics in the anomalous regime follows $E \propto \text{deformation}^a$, with $1 < a < 2$ and results from a complex interplay of in-plane energy relaxation with non-bonded and bending energy penalties. This response can be clearly observed in Fig. 9, where a 20-walled nanotube is considered. It is apparent form the figure that the harmonic regime previous to rippling only holds in a small neighborhood of the straight configuration. When plotted in a log-log scale, the energy evolution clearly displays two distinct regimes characterized by the slopes 2 (harmonic) and $a = 1.56$ (rippled). This results in a nonlinear moment-curvature relationship, and an elastic modulus that depends with deformations [3]. Simulations with larger tubes suggests that the larger the MWCNT is, the

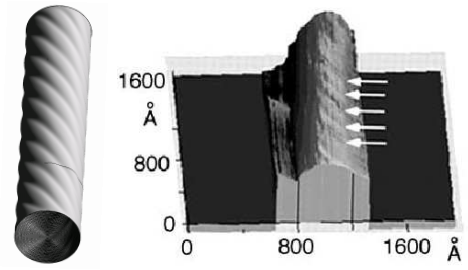


Figure 10. Torsional rippling: simulation of a 34-walled CNT, and experimental observation suggesting a pattern of torsional rippling, although originally interpreted as bending rippling [15].

smaller the harmonic regime is. It should be stressed that all these phenomena are reversible, although a small hysteresis loop is observed upon unloading in the vicinity of the cross-over region.

Torsional rippling is also predicted by the simulations, with a similar anomalous elastic behavior. Unlike bending rippling, this behavior has not been reported in the literature, although some published images [15] seem to suggest torsional rippling in the view of the simulations (see Fig. 10). The experimental image shows ripples that are not orthogonal to the axis of the tube, thus suggesting that the nanotube is subjected to torsion or combined bending and torsion. These results are particularly relevant in view of the proliferation of nanoscale devices in which thick MWCNTs act as rotational springs (see for example [29]).

Further understanding beyond simulations of this complex nonlinearly elastic response is needed. For instance, the systematic dependence of the exponent a on the deformation mode or the number of walls is not clear. Also, a simple analysis in the spirit of [24] that would illuminate on how do the different parameters of the system affect the anomalous response is missing.

4. Outlook

We have presented a systematic approach in the spirit of finite crystal elasticity and the Cauchy-Born rule to bridge atomistic descriptions of crystalline films and continuum mechanics. We have briefly discussed how to understand the convergence of atomistic and continuum models in this setting, and reviewed the application of the theory to study the nonlinear mechanics of carbon nanotubes. In particular, an anomalous elastic response of thick MWCNTs has been reported. We conclude by

outlining some avenues of current and future research in the field of continuum and multiscale modelling of nanotubes.

Coupling with atomistics. Despite we have seen that atomistic-based nonlinear elasticity goes a long way in describing the mechanics of carbon nanotubes, some phenomena such as fracture require the explicit tracking of individual atoms, at least in some region. Coupled ECB continuum-atomistic modelling of fracture of carbon nanotubes has been reported in [42].

Multiphysics analysis. As we have mentioned, the relevance of mechanics in nanotube science and technology is largely due to the strong function of other properties such as electrical conductance or chemical reactivity on deformation. Coupling continuum mechanics with atomistic methods capable of resolving the electronic structure (at fixed geometry) is an obvious opportunity [1] to further exploit the efficiency of continuum simulations. See [21, 28] for recent work along these lines.

Mesoscopic models. The effective analysis and design of nano-devices ultimately needs simple yet accurate models amenable to the engineering practice. The atomistic-based continuum mechanics constitute a first step towards such mesoscopic models. Some efforts in formulating mesoscopic descriptions can be found in [9, 43].

Theoretical underpinnings of the continuum-discrete connection. We have seen that a number of justified and even convergent continuum models can be associated with a given atomistic model. With the proliferation of continuum models equivalent in some sense to discrete models, new theoretical tools to assess their performance would be greatly beneficial.

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